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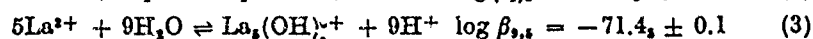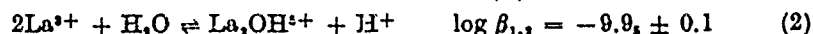
Studies on the Hydrolysis of Metal Ions

## Part 35. The Hydrolysis of the Lanthanum Ion, La³+

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The hydrolysis equilibria of the La(III) ion have been studied at 25°C by hydrogen ion concentration measurements, using a glass electrode. The total [La(III)] was varied between 0.1 and 1.0 M, whilst the concentration of the ClO_4^- ion was held constant at 3 M by the addition of $LiClO_4$. The data, which indicate a slight hydrolysis in the log h range -6.5 to -8.1, can be explained by assuming the equilibria

$$La^{3+} + H_2O \rightleftharpoons LaOH^{2+} + H^+ \qquad \log \beta_{1,1} = -10.1 \pm 0.1 \qquad (1)$$

$$2La^{3+} + H_2O \rightleftharpoons La_2OH^{5+} + H^+ \qquad \log \beta_{1,2} = -9.9_5 \pm 0.1 \qquad (2)$$

$$5La^{3+} + 9H_2O \rightleftharpoons La_5(OH)_9^{6+} + 9H^+ \qquad \log \beta_{9,5} = -71.4_5 \pm 0.1 \qquad (3)$$

Equally good agreement with the data (see Fig. 1) is obtained by replacing equilibrium (3) with

$$6La^{3+} + 10 H_2O \rightleftharpoons La_6(OH)_{10}^{8+} + 10 H^+ \qquad \log \beta_{10,6} = -78.7_5 \pm 0.1 \qquad (4)$$
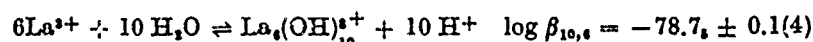
No other mechanism, involving the formation of only three hydrolysed species, could be found which would explain the experimental data.

The experimental conditions necessary for accurate results to be obtained, when the hydrolysis equilibria must be studied in poorly buffered solutions, are discussed in some detail.

The first quantitative study on the hydrolysis equilibria of the La(III) ion was carried out in 1916 by Vesterberg [1], who measured the distribution ratio of acetic acid between lanthanum acetate solutions and ether. By taking into account the acidity and distribution constants of acetic acid, Vesterberg was able to calculate the hydrogen ion concentration in the lanthanum acetate solutions from the distribution data. The results were explained by assuming the equilibrium

$$La^{3+} + H_2O \rightleftharpoons LaOH^{2+} + H^+ \qquad \beta_{1,1}^- = [LaOH^{2+}] h [La^{3+}]^{-1} \qquad (1)$$
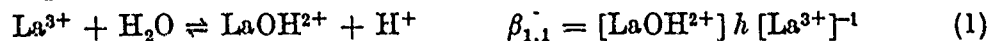
and Vesterberg found $\beta_{1,1}$ to be approximately equal to the acidity constant of the NH_4^+ ion (thus the value of log $\beta_{1,1}$ is around -9.4).
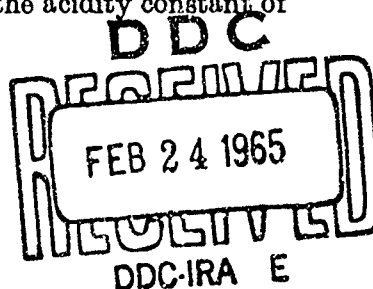
During the last fifteen years interest in the chemistry of the rare earths has revived and several attempts have been made to find the composition of the hydrolysis products of La(III).

In 1946 Moeller [2] measured the acidity of a series of purified lanthanum sulfate solutions at 25°C using a glass electrode. The data for $[La(III)] \leq 0.01M$ could be well explained by equilibrium (1) with $\log \beta_{1,1} = -10$. At higher concentration of La(III), however, the calculated $\beta_{1,1}$ values showed a tendency to increase, from which Moeller concluded that additional hydrolysis products become important at high values of [La(III)].

In 1953 Wheelwright, Spedding and Schwarzenbach [3] titrated with NaOH, using a glass electrode, a 0.01 M LaCl$_3$ solution containing an excess of HCl at 25°C. On the basis of these measurements they have estimated $\log \beta_{1,1} = -8.4$. Similar measurements were also made in 1953 by Busey and Cowan [4], and Kraus [4] has used their data to estimate $\log \beta_{1,1} = -8.3$.

In 1957 Lewis [5] measured the solubility of La$_2$O$_3$ in solutions of $\log h$ varying between -7.5 and -10.5 and concluded that extensive hydrolysis occurs in this acidity range.

Symbols often used in the text

h = hydrogen ion concentration at equilibrium
H = analytical excess of hydrogen ions $= [ClO_4^-] - 3B - [Li^+]$
B = total concentration of La(III)
Z = average number of hydrogen ions set free per lanthanum atom
     $= (h-H) B^{-1}$
p = number of OH groups bound to hydrolysed species
q = number of La atoms present in hydrolysed species
b = concentration of La^{3+}
K_p = equilibrium constant for formation of all species containing p OH groups
$\beta_{p,q}$ = equilibrium constant for formation of La$_q$(OH)$_p$

CHOICE OF EXPERIMENTAL CONDITIONS

Preparation of the solutions. In the present work the hydrolysis equilibria were studied at 25°C by measuring the hydrogen ion concentration in a series of lanthanum perchlorate solutions of varying acidity. Preliminary experiments have indicated that the hydrolysis becomes appreciable at $\log h < -6.5$, and that only a small part of La^{3+} can be transformed to hydrolysis products before precipitation starts. It was found that in clear solutions the highest value of Z cannot exceed 0.02, thus we must confine our work to solutions of a very low buffer capacity. Under such experimental conditions great care is required to avoid contamination of the solutions to be studied by foreign protolytes, *e.g.* those inevitably present at small concentrations in strong base solutions (carbonate, borate, silicate and aluminate).

In favorable cases, when the hydrolysis equilibria can be studied in solutions of $\log h > -5$, the preparation of hydrolysed solutions is simple. One

may start with a solution of such a high h that the hydrolysis is negligible, and add successively increasing amounts of a strong base solution. If log h $>$ —5, then the impurities, most likely to be introduced with a strong base solution, do not cause an appreciable error because all of them are present in the unhydrolysed form. For this reason also NaHCO$_3$ can be used, instead of NaOH, as was suggested by Hedström [6].

On the other hand, when the hydrolysis becomes appreciable at log h < —5 and only low Z values can be attained, the measured value of h may be seriously in error if the hydrolysed solution is prepared by adding a strong base, because at these low acidities the impurities are protolysed to a considerable extent. Clearly the lower the values of Z and h that are studied, the greater becomes the error caused by the protolysis of the contaminants.

We have made a number of attempts to purify Ba(OH)$_2$ (which is to be preferred to NaOH) by repeated recrystallizations in a N$_2$ atmosphere. The carbonate content could be much reduced by three recrystallizations (though it was still too high for our purposes), but the concentration of the other impurities (silicates, *etc.*) was thereby increased somewhat, because of prolonged contact with glass surfaces.

It should be added, that at log h < —11 the impurities present in a strong base solution again have a negligible influence on h, because all of them, with the exception of silicates, are mainly present in the completely hydrolysed form.

The method finally adopted for preparing hydrolysed lanthanum solutions does not require a strong base. We have started from a slightly acid lanthanum perchlorate solution (log $h \sim$ —4, measured with an indicator paper) which was freed of CO$_2$ by passing purified nitrogen through it. The hydrogen ion concentration of this initial solution was decreased by adding an excess of freshly ignited La$_2$O$_3$; rapid equilibration was ensued by stirring for several hours at 90°C. Finally the excess La$_2$O$_3$ was removed by careful filtration. All the operations were carried out in an atmosphere of nitrogen.

Using this method, the introduction of foreign substances is avoided and the maximal value of Z in the final solution can be approached closely, by stirring with the solid for a sufficiently long time. (In the cases studied hitherto equilibrium was attained within 24 h). Moreover, since log h never becomes less than —8 (see Fig. 1) no significant amounts of impurities are brought into the solution by contact with glass surfaces. Nevertheless, Jena glass is to be preferred to Pyrex to diminish dissolution of boric acid.

Methods similar to that described above have proved to be of great value for the preparation of hydrolysed solutions of a number of metal ions, as Ag$^+$ (Ref.[7]), Cd^{2+}, Ni^{2+}, Ce^{3+} and Y^{3+}, in a state of high purity.

The composition of the solutions. The main prerequisite for obtaining accurate data on hydrolysis equilibria is to work in solutions of appreciable buffer capacity. This requirement could be realized in the present case by studying rather concentrated lanthanum solutions: values of B ranging from 0.1 to 1 M have been investigated. In each series of experiments (except two which were done for special purposes) the [ClO$_4^-$] was kept constant at 3 M by adding the inert salt LiClO$_4$.

On the basis of measurements made by one of us (G.B.) it may be concluded that when the ratio $r = z_i c_i / [ClO_4^-]$ exceeds about 0.1 (z_i = charge of reacting cation, c_i = concentration of the reacting cation) the deviation of the activity factors of the reacting ions from constancy becomes appreciable. Consequently, the methods of calculation worked out for treating data obtained in an inert medium ($r < 0.1$) cannot be applied to our measurements which were made in solutions for which r had high values.

One can, however, use the "self-medium" approach proposed by Hietanen and Sillén [8]. The principle of this method is that data obtained at different values of B are regarded separately. In each series of measurements, where B is kept constant and low values of Z are studied, the variation of the activity factors is negligible because the composition of the solution changes only slightly. In consequence, the law of mass action expressed in terms of concentrations can be applied to the data to evaluate the number of OH groups bound to the reaction products, p. Obviously, the number of metal ions present in the reaction products, q, cannot be obtained straightforwardly by the self-medium method, because in each series of experiments the concentration of the free (unhydrolysed) metal ions, b, is very close to B.

The self-medium method is used generally to detect the formation of species $Me_q(OH)_p$ (Me = metal ion) with a high value of q/p, whereas the main body of information is obtained with the inert medium method. For such an unfavorable case as the La(III) ion an exact treatment of the data is possible, at present, only by the self-medium method.

It will be shown in the "Composition of the hydrolysis products" section that, although the unknown variation of the activity factors introduces some uncertainty, plausible arguments can be given for estimating the probable values of q.

THE METHOD OF MEASUREMENTS.

In each series of measurements, which were carried out as potentiometric titrations, B was kept constant; the B values studied ranged from 0.0973 to 1.111 M. The measurements were performed by starting with a solution ("S_0") containing an initially unknown deficit of hydrogen ions ($-H_0$) and adding to it successively increasing volumes (V_T ml) of another solution ("T") containing about 0.02 to 0.10 M $HClO_4$ ($= H_T > -H_0$).

Since the hydrolysis of La^{3+} proved to be quite negligible for $\log h > -5$ the hydrogen ion concentration in solution T is equal to the analytical excess of hydrogen ions. Both S_0 and T were prepared from a partially hydrolysed lanthanum perchlorate stock solution which was itself prepared as described in the previous section.

The concentration of ClO_4^- in all the solutions studied (except two, see below) was made up to 3.00 M by the addition of $LiClO_4$. $LiClO_4$ was chosen as the "solvent salt" because, in contrast to $NaClO_4$, it can be purified easily by recrystallisation. In the lanthanum stock solution $[ClO_4^-]$ was set approximately equal to 3 [La(III)] which is near to the true $[ClO_4^-] = 3.000 + H_0$. The maximal value of H_0 was -0.017 M (at $B = 1$ M), therefore the deviation of $[ClO_4^-]$ from 3 M has never exceeded 0.6 %.

The solutions thus had the general composition

B M La(III), H_s M H$^+$, $(3.000 - 3B - H_s + H_0)$ M Li$^+$, $(3.000 + H_0)$ M ClO$_4^-$ = solution S

where H_s, the analytical excess of hydrogen ions, is equal to

$$H_s = \frac{V_0 H_0 + V_T(H_T + H_0)}{V_0 + V_T} = H_0 + \frac{V_T H_T}{V_0 + V_T} \qquad (2)$$

In (2) H_T denotes the hydrogen ion concentration in solution T, calculated by assuming H_0 to be negligible, V_0 is the volume of S$_0$ and V_T is the volume of T added.

A few series of measurements were made with solutions in which B was 0.1 M and [Li$^+$] was 0.01 M. The purpose of these measurements was to check whether any appreciable amounts of impurities were introduced by adding LiClO$_4$. A number of additional measurements were also made with solutions in which B was 1.111 M and [Li$^+$] was 0.1 M, in order to get some idea on the influence of the counter ion concentration on the numerical values of the equilibrium constants. The solutions containing 0.31 M and 3.43 M ClO$_4^-$ were studied in the same way as solutions S.

The hydrogen ion concentration of solutions S was measured by means of the cell

$$- \text{GE} \,/\, \text{solution S} \,/\, \text{SE} + \qquad (A)$$
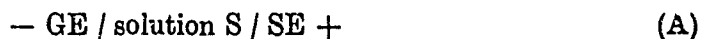
where GE denotes a glass electrode and SE is the reference half-cell

$$/3.000 \text{ M LiClO}_4/2.990 \text{ M LiClO}_4, \ 0.010 \text{ M AgClO}_4/\text{AgCl, Ag}$$

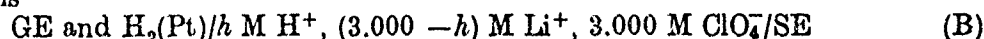The emf of cell (A) at 25°C can be written

$$E = E_0 - 59.15 \log h - 59.15 \log f(\text{H}^+) + E_j(h,B) \qquad (3)$$

where E_0 is a constant and h is the hydrogen ion concentration at equilibrium. $f(\text{H}^+)$ denotes the activity factor of H$^+$. The standard state is defined so that $f(\text{H}^+)$, as well as the activity factors of the other reacting species, tend to unity when the composition of the solution approaches 3 M LiClO$_4$. For each series of measurements, when B was kept constant, it is certainly a good approximation to assume that $f(\text{H}^+)$ = constant, consequently we may write
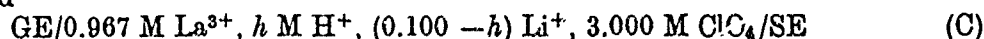
$$E = E_0' - 59.15 \log h + E_j(h,B) \qquad (4)$$

where E_0' is a function of B.

In (3) and (4) $E_j(h,B)$ denotes the liquid junction potential at the junction solution S/3 M LiClO$_4$. $E_j(h,B)$ was determined by measuring the emf of the cells

$$\text{GE and H}_2(\text{Pt})/h \text{ M H}^+, (3.000 - h) \text{ M Li}^+, 3.000 \text{ M ClO}_4^-/\text{SE} \qquad (B)$$

and

$$\text{GE}/0.967 \text{ M La}^{3+}, h \text{ M H}^+, (0.100 - h) \text{ Li}^+, 3.000 \text{ M ClO}_4/\text{SE} \qquad (C)$$

in the h range 0.01 to 0.1 M.

From the emf data with cell (B) we have calculated $E_j(h,0) = -15.8\,h$ mV, and from those with cell (C) $E_j(h, 0.967) = -20.0\,h$ mV. Thus up to $h = 0.01$

M no appreciable error is made when $E_j(h,0)$ is used for the entire B range $0.1-1.0$ M.

It was necessary to use the two cells (B) and (C), because in solutions where $[La^{3+}] \geq 0.1$ M the hydrogen electrode was found to give potentials which drifted at the rate of several mVs per hour. Moreover, when two hydrogen electrodes were immersed in the same lanthanum solution they differed by 40 to 60 mV. A similar difficulty was encountered previously in solutions of other tervalent ions such as In^{3+} and Sc^{3+}. The failure of hydrogen electrode in these solutions may be caused by the strong adsorption of tervalent ions on the platinized platinum surface, which thus looses its catalytic activity.

The hydrolysis of La(III) could not be studied by the quinhydrone electrode, because quinone is not stable in solutions of $\log h < -7$. The glass electrodes were calibrated against the quinhydrone electrode. When a glass and a quinhydrone electrode were immersed in the same solution and $\log h$ was varied from -2 to -7, the difference between the potentials of the glass and the quinhydrone electrode was found to be constant within ± 0.2 mV.

Each of the potentiometric titrations may be divided into two parts. The measurements in the low acidity range ($\log h < -5$, part I) were made to determine h in hydrolysed solutions, whereas the E data at higher acidities (part II) served to calculate H_0 and E_0'. The value of H_0 was obtained by means of a Gran plot [9], which was constructed on the basis of the E values

Table 1. A series of measurements with $B = 0.0973$ M

$[La(III)] . 9.73 \times 10^{-2}$ M, $[Li^+] : 2.700$ M, $[ClO_4^-] : 3.00$ M $= S_0$, $V_0 = 50.00$ ml
$[La(III)] : 9.73 \times 10^{-2}$ M, $H_T : 2.000 \times 10^{-2}$ M, $[Li^+] : 2.680$ M, $[ClO_4^-] : 3.00$ M $= T$

V_T ml	E mV	$-\log h$	$BZ \times 10^3$ M	E_0' mV
0.00	421.4	8.056	1.718	
0.70	420.5	8.040	1.442	
1.20	419.6	8.025	1.249	
1.70	418.2	8.001	1.060	
2.20	416.1	7.966	0.875_1	part 1
2.60	413.1	7.915	0.729_5	
2.90	409.2	7.850	0.621_7	
3.10	405.5	7.787	0.550_5	
3.40	398.7	7.672	0.444_8	
3.70	392.2	7.565	0.340_0	
4.00	383.3	7.412	0.236_7	
4.20	366.5	7.128	0.168_4	
5.00	178.7	4.000		119.5
5.50	156.2	3.579		122.0
6.00	144.2	3.372		122.2
7.00	130.2	3.136		122.2 part II
8.00	121.4	2.983		122.4
9.00	115.0	2.875		122.4
10.00	110.1	2.792		122.4

$E_0' = 122.3 \pm 0.1$ mV
$H_0 = -(1.718 \pm 0.005) \times 10^{-2}$ M

obtained in part II by taking into account (2) and (4). Then we could calculate E_o' for each experimental point of part II with (4). E_o' proved to be constant at least within $\pm$ 0.2 mV, typical results are shown in Table 1. Finally, the values of H_o and E_o' thus obtained, were used for the calculation of log h and Z corresponding to the experimental points of part I.

MATERIALS AND ANALYSIS

Lanthanum perchlorate solutions were made from La_2O_3 of 99.997 % purity supplied by Lindsay Chemical Division, West Chicago, USA. According to the manufacturer the maximum amount of rare earth impurities in this material is 0.0025 %, consisting mainly of praseodymium oxide. No Fe(III)-, heavy metal-, Cl^- or SO_4^{2-} ions could be detected in the batches of La_2O_3 used, each of these batches, however, contained some carbonate.

The method employed to prepare partially hydrolysed lanthanum perchlorate solutions has been described in the "Preparation of the solutions" section. We shall discuss here only two important experimental details: 1) the preparation of carbonate-free La_2O_3 and 2) the removal of excess La_2O_3.

1) It was found that a La_2O_3 preparation, which has been kept in contact with air, must be ignited to 1 100°C to expel the last traces of carbonate. In materials ignited at 900°C, the temperature generally recommended for analytical purposes, appreciable amounts of carbonate could be detected. The ignition should be made preferably in a porcelain crucible, because the carbonate in La_2O_3 seems to react with platinum at high temperature. Avoidance of platinum is especially important if La_2O_3 is prepared by decomposing lanthanum oxalate.

2) It is essential to add some filter paper pulp before filtering the lanthanum perchlorate solution which contains suspended La_2O_3, because (if this precaution is not taken) the finest La_2O_3 particles are likely to go through a sintered glass filter of porosity G4. We have used each time, one half of a "Whatman ashless tablet" (Balstone Ltd, England).

To test the filter paper pulp for impurities a suspension was made containing one tablet in 10 ml distilled water. No Cl^- or heavy metal ions could be detected in the filtrate from this suspension, and the filtrate, which had the same pH as the distilled water, did not contain acidic or alkaline impurities in significant amounts.

The filtered lanthanum perchlorate solutions were regularly examined for turbidity during several weeks (in one case during three months) but no suspended La_2O_3 particles could be detected. In order to detect turbidity the solution was illuminated by an intense and thin light beam in a dark room.

The [La(III)] in the stock solutions was determined by precipitating lanthanum oxalate, then dissolving this in 1 M H_2SO_4 and oxidizing it with $KMnO_4$. Essentially the procedure proposed by Kolthoff and Elmquist [10] was followed. The results were reproducible within $\pm$ 0.1 %. The $KMnO_4$ solution was standardised (*via* a $Na_2S_2O_3$ solution) against KIO_3, which serves as a primary standard in this laboratory.

An approximate value for the deficit of hydrogen ions ($[ClO_4^-]-3$ [La(III)]) in the stock solution was found by adding a measured volume of a standardised $HClO_4$ to a weighed amount of the lanthanum solution and titrating this mixture with NaOH using methyl-red as indicator.

LiClO₄ solutions were made from Li_2CO_3 and $HClO_4$, both of p.a. quality, supplied by Baker Chemical Corporation. First a saturated solution of $LiClO_4$ was prepared at room temperature, and to it was added a small excess of Li_2CO_3. The slightly alkaline solution (pH ~ 8) was left to stand overnight and then the precipitate that formed, which consisted mainly of FeOOH and $SiO_2(H_2O)_x$, was removed by filtration. The pH was then decreased to 3 by the addition of dilute $HClO_4$, the solution was boiled to expel CO_2 and to concentrate it further. Then, the slightly acidic solution was slowly cooled to 0°C and the crystals of $LiClO_4$ which formed were filtered off. The $LiClO_4$, which contained traces of $HClO_4$, was twice recrystallized from water. No Cl^-, SO_4^{2-} or Fe(III) could be detected in a 4 M $LiClO_4$ stock solution.
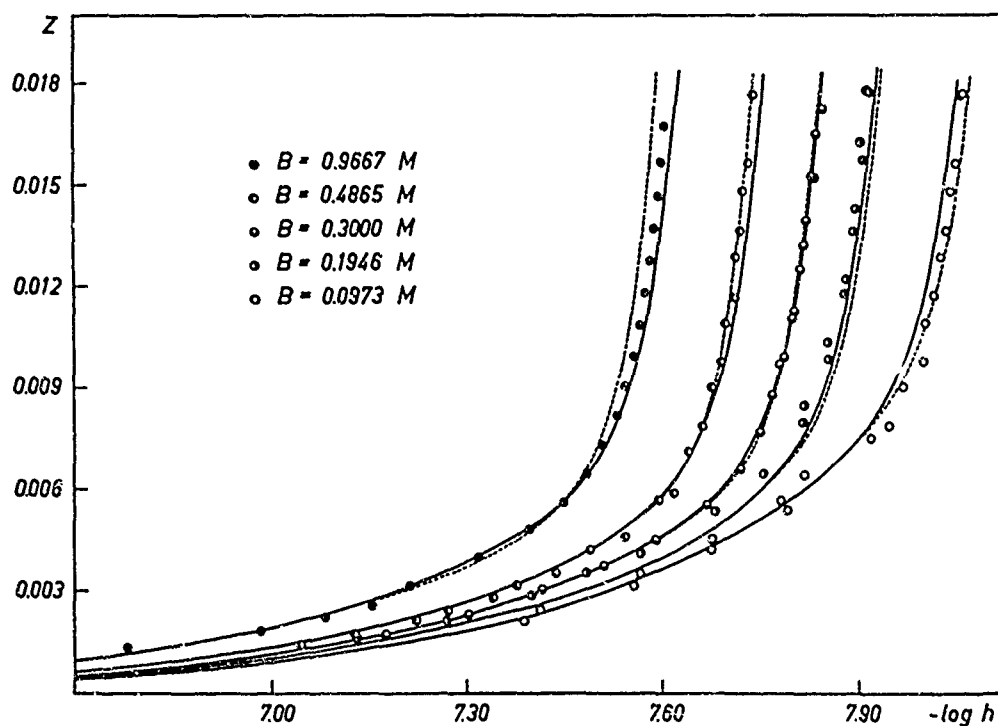
Fig. 1. Z, the average number of hydrogen ions set free per lanthanum, as a function of $-\log h$. The full-drawn curves have been calculated with $-\log \beta_{1,1} = 10.1$, $-\log \beta_{1,2} = 9.95$ and $-\log \beta_{2,2} = 71.45$. The dotted curves have been calculated with the same $\beta_{1,1}$ and $\beta_{1,2}$ values and $-\log \beta_{10,6} = 78.75$.

A series of experiments was made with $LiClO_4$ which had been recrystallized a third time using platinum vessels. The $Z(\log h)_B$ data found with this preparation coincided with those obtained when twice recrystallized $LiClO_4$ was used. We may thus conclude that no appreciable amounts of protolytes were dissolved from glass surfaces when the $LiClO_4$ was prepared.

The concentration of the stock solution was determined by passing a weighed amount through a cation exchanger in the hydrogen form and titrating the eluate with standardised NaOH.

AgClO₄ solutions were made using Merck p.a. $AgNO_3$. A great excess of 11 M $HClO_4$ was added to a concentrated solution of $AgNO_3$, and HNO_3 was expelled, together with a large part of the excess $HClO_4$, by evaporating the mixture nearly to dryness. $[Ag^+]$ was determined potentiometrically with a NaCl solution made from a Br^- and water-free NaCl preparation.

HClO₄ solutions were standardised against $KHCO_3$ and Tl_2CO_3. The results obtained with these standard substances agreed within $\pm$ 0.1 %.

NaOH solutions were titrated with standardised $HClO_4$.

Experimental details of the emf measurements. All emf measurements were carried out at $25.00 \pm 0.01°C$ in a paraffin oil thermostat. The cell arrangement was similar to that described by Forsling, Hietanen and Sillén [11]. The titration vessel was filled with N_2 before the starting solution was introduced, and a vigorous stream of N_2 was passed through solution S during the measurements. The nitrogen, which was taken from a cylinder, was purified and presaturated by passing it through 2 M NaOH, then water and finally 3 M $LiClO_4$.

Table 2. Survey of measurements.

$B = 0.967$ M

$Z \times 10^3$, $-\log h$. 16.69, 7.604; 15.66, 7.599; 14.66, 7.594; 13.68, 7.587; 12.71, 7.581; 11.77, 7.572; 10.84, 7.564; 9.91, 7.554; 9.03, 7.542; 8.15, 7.528; 7.29, 7.506; 6.47, 7.483; 5.61, 7.447; 4.79, 7.395; 3.99, 7 315; 3.20, 7.211; 2.55, 7.153; 2.27, 7.070; 1.82, 6.981; 1.36, 6.778.

$B = 0.486_4$ M

$Z \times 10^3$, $-\log h$. Series a. 17.66, 7.738; 15.63, 7.731; 13.63, 7.719; 11.68, 7.709; 9.76, 7.689; 7.89, 7.664; 6.03, 7.616; 4.57, 7.544; 3.50, 7.435; 2.79, 7.341; 2.08, 7.222; 1.38, 7.043.

Series b. 17.66, 7.738; 14.82, 7.723; 12.84, 7.711; 10.90, 7.696; 9.00, 7.674; 7.13, 7.638; 5.36, 7.594; 4 21, 7.488; 3.14, 7.374; 2.44, 7.265, 1.73, 7.126.

$B = 0.300_0$ M

$Z \times 10^3$, $-\log h$. Series a. 16.45, 7.834; 15.24, 7.827; 13.95, 7.819; 12.52, 7.811; 10.99, 7.797; 9.87, 7.785; 8.76, 7.770; 7.65, 7.750; 6.56, 7.721; 5.48, 7.672; 4.42, 7.591; 3.71, 7.510; 3.01, 7.415; 2.32, 7.302; 1.63, 7.173. Series b. 17.21, 7.836; 15.18, 7.829; 13.18, 7.817; 11.23, 7.799; 9.69, 7.778.

$B = 0.194_4$ M

$Z \times 10^3$, $-\log h$. Series a. 17.73, 7.917; 15.69, 7.907; 13.69, 7.893; 11.74, 7.878; 9.83, 7.853; 7.94, 7.814; 6.46, 7.755; 5.36, 7.680; 4.28, 7.566; 3.57, 7.481; 2.86, 7.396; 2.15, 7.268.

Series b. 17.75, 7.915; 16.22, 7.905; 14.22, 7.896; 12.20, 7.881; 10.33, 7.854; 8.44, 7.814; 2.09, 7.127.

$B = 0.097_3$ M

$Z \times 10^3$, $-\log h$. Series a. 17.66, 8.061; 15.62, 8.049; 13.63, 8.034; 11.67, 8.015; 9.76, 7.991; 7.86, 7.946; 5.30, 7.790; 4.21, 7.674; 3.14, 7.554; 2.08, 7.378;

Series b. 17.66, 8.056; 14.82, 8.040; 12.84, 8.025; 10.89, 8.001; 8.99, 7.966; 7.50, 7.915; 6.39, 7.850; 5.66, 7.787; 4.57, 7.672; 3.49, 7.562; 2.43, 7.412.

$B = 1.11_1$ M, $[ClO_4^-] = 3.43_3$ M

$Z \times 10^3$, $-\log h$. Series a. 17.87, 7.579; 16.98, 7.577; 16.10, 7.572; 14.40, 7.562; 12.77, 7.552; 11.20, 7.542; 9.68, 7.527; 8.23, 7.503; 6.81, 7.431; 5.46, 7.444; 4.13, 7.369; 3.49, 7.309; 2.86, 7.222; 2.24, 7.112; 1.64, 6.977; 1.04, 6.683.

Series b. 17.81, 7.586; 16.50, 7.581; 15.19, 7.576; 13.53, 7.564; 11.93, 7.552; 10.38, 7.538; 8.90, 7.552; 7.46, 7.501; 6.00, 7.471; 4.74, 7.417; 3.95, 7.361; 3.32, 7.293; 2.81, 7.217; 2.44, 7.155; 2.07, 7.089; 1.70, 7.008, 1.34, 6.881; 0.98, 6.626; 0.74, 6.296.

$B = 0.100_0$ M, $[ClO_4^-] = 0.31$ M

$Z \times 10^3$, $-\log h$. 17.92, 8.039; 17.26, 8.033; 16.41, 8.023; 15.36, 8.012; 14.33, 7.998; 13.32, 7.978; 12.33, 7.959; 11.36, 7.939; 10.41, 7.910; 9.66, 7.883; 8.92, 7.853; 8.38, 7.831; 8.02, 7.809; 7.48, 7.783; 6.77, 7.743; 6.90, 7.699; 5.56, 7.665; 5.05, 7.619; 4.55, 7.565; 4.05, 7.503; 3.55, 7.434, 3.06, 7.332; 2.58, 7.183; 1.93, 6.997; 1.62, 6.644.

Type 1190−80 Beckman glass electrodes were used; in our solutions, these came to a steady state within 10 min, and gave potentials constant within ± 0.2 mV.

A number of lanthanum stock solutions were prepared from different batches of La_2O_3; the $Z(\log h)_B$ data obtained with solutions of different origin have agreed within the limits of experimental uncertainty (± 0.003 log h units).

Ag, AgCl electrodes were prepared according to Brown [11].

E was measured with a Radiometer PHM 4 valve potentiometer, this instrument was calibrated against a Leeds & Northrup type K_3 compensator.

THE COMPOSITION OF THE HYDROLYSIS PRODUCTS

The $Z(\log h)_B$ data, which form the basis of the following calculations, are summarized in Table 2 and are represented graphically in Fig. 1.

The determination of the composition of the hydrolysis produ;ts and the evaluation of the corresponding equilibrium constants will be carried out in three steps. In the first (section I), each set of data pertaining to a particular value of B will be treated by the self-medium method. Using this method we can calculate for each value of B studied, the number of OH groups bound to the hydrolysis products, p, and the formation constants of species having a common p, $K_p = K_p(B)$.

In the second step (section II), probable values are derived for the number of lanthanum atoms present in the hydrolysed species, q, by analysing the $K_p(B)$ functions. Lastly all the $Z(\log h, B)$ data are considered simultaneously and as a final check they are compared with normalised model functions.

I. The calculation of p. Treatment of the data by the self-medium method

When we consider a set of data obtained at a constant B and take into account that in our solutions the maximal value of Z never exceeds 0.02, then, without introducing any appreciable error, we may simplify the *preliminary* calculations by using the approximation

$$[La^{3+}] = b \cong B = \text{constant} \tag{5}$$

Assuming the formation of a series of reaction products with the general composition $La_q(OH)_p^{(3q-p)+}$, the concentration of hydrogen ions set free by hydrolysis, BZ, is expressed by the equation

$$BZ = \sum_p \sum_q p\,[La_q(OH)_p] = \sum_p \sum_q p\beta'_{p,q}\,b^q h^{-p}\,f^{-1}(p,q)f^q(La^{3+})f^{-p}(H^+) \tag{6}$$

where the formation constant of $La_q(OH)_p$ is denoted by

$$\beta'_{p,q} = [La_q(OH)_p]h^p b^{-q} f(p,q)f^p(H^+)f^{-q}(La^{3+}) \tag{7}$$

p and q represent integers, and f is the symbol for the activity factors.

In each series of measurements ($B = $ constant) the activity factors may be regarded as constants and we may use approximation (5), thus (6) can be written

$$BZ \simeq \sum_p \sum_q p h^{-p} B^q \beta_{p,q} = \sum_p p h^{-p} K_p \tag{8}$$

where

$$\beta_{p,q} = \beta_{p,q}(B) = [La_q(OH)_p]h^p b^{-q} \tag{9}$$

and

$$K_p = K_p(B) = \sum_q B^q \beta_{p,q} \tag{10}$$

K_p is the formation constant of the species containing p OH groups. Complexes having the same value of p but different values of q may be called homoligandic complexes.

We first tried to explain our data in the simplest way by assuming that all hydrolysed species are homoligandic. To test this hypothesis we compared

the experimental data $BZ(\log h)_B$ with the normalised[13] form of (8), $\varphi_p(\log w)$, calculated for the case where p has a single value, P

$$\varphi_p = BZ = PK_p h^{-P} = Pw^P; \; \log w = \frac{\log K_P}{P} - \log h \qquad (11)$$

Values of P ranging from 1 to 12 were inserted in (11), but, over the entire BZ range studied, no satisfactory agreement with any set of values of $Z(\log h)_B$ was found. When $Z \leq 0.01$, however, the data for each value of B seemed to fit the function φ_1, indicating the predominance of species $La_q(OH)$. No certain conclusions concerning the composition of the species which become important when $Z > 0.01$ can be drawn on the basis of (11).

The predominance of monoligandic species at $Z < 0.01$ can be shown very clearly by calculating (using approximation (5)) the average number of OH groups bound to the reaction products, $\bar{p}$.

$$\bar{p} = \frac{\Sigma p[La_q(OH)_p]}{\Sigma[La_q(OH)_p]} = BZ \left[2.303 \int\limits_{\log h}^{\infty} BZ \; d \log h \right]^{-1} \qquad (12)$$

Eqn. (12) is derived from (8) by considering that $Z \to 0$ as $\log h \to \infty$. The value of $\int\limits_{\log h}^{-7} BZ \; d\log h$ was calculated by means of the trapezoidal formula, using a plot of BZ versus $-\log h$. Smooth curves were drawn through the experimental points and the integration was done with intervals of 0.05 log h unit. In order to eliminate errors introduced by drawing smooth curves, another integration was also performed taking the experimental points directly (i.e. with unequal intervals). The results of the two integrations coincided within the limits of experimental uncertainty.

The evaluation of the residual integral $2.303 \int\limits_{-7}^{\infty} BZ \; d\log h$ was carried out by extrapolation. The three lowest experimental $Z(\log h)_B$ values were fitted to φ_1 (cf. (11)), which was assumed to represent the experimental points at those high acidities where no data were available. Another extrapolation was also made by using φ_2 instead of φ_1. The areas under the curves were calculated by

$$\int\limits_0^{w_0} \varphi_p \frac{dw}{w} = \int\limits_0^{w_0} Pw^{(P-1)} \cdot dw = w_0^P$$

where w_0 is the value of w corresponding to $h = 10^{-7}$. The magnitude of the residual integral was, of course, influenced to some extent by the choice of the extrapolation function, but at $\log h < -7.3$ the values of $\int\limits_{\log h}^{\infty} BZ \; d\log h$ calculated with φ_1 and φ_2 agreed within 3 %.

The results of our calculations are shown in Fig. 2 where $\bar{p}$ is plotted versus $-\log h$. It can be seen that, for each value of B, a range of $\log h$ of considerable width can be found where $\bar{p}$ is equal to 1.00 ± 0.05. In this range of log h, $K_1 \cong BZh$ was calculated for each experimental point. The calculated K_1 values have shown no appreciable trend with h. The probable values of the constants are summarised in Table 3.
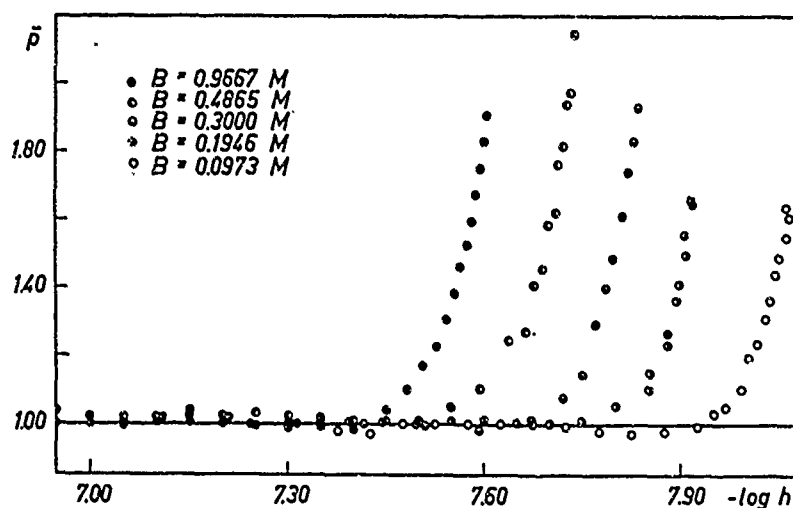
Fig. 2. $\bar{p}$ (eqn. (12)), the average number of OH groups bound to the complexes, as a function of $-\log h$.

Fig. 2 shows moreover that, as $\log h$ approaches the value where precipitation starts, $\bar{p}$ increases steeply and attains values exceeding 2. This suggests that species with $p > 2$ are also formed in appreciable amounts at each of the values of B studied.

In order to explain the data obtained at higher values of Z the hypothesis was made that, in addition to La^{3+} and La_qOH, a further species $La_{q'}(OH)_{p'}$ is present in our solutions (in these formulas p' denotes a constant whereas q and q' may take a series of values). This hypothesis was tested by comparing the experimental data, recalculated to the form $\log (BZh)$ *versus* $(-\log h)_B$, with a group of functions obtained by normalizing (3). Assuming the formation of two species with $p = 1$ and $p = p'$ (8) can be written

$$BZ = K_1 h^{-1} + p' K_{p'} h^{-p'} \tag{13}$$

Table 3. Survey of the calculated K_1 and p' values.

B M	K_1 M^2	p' eqns. (5) and (16)	p' eqn. (17)
1.11$_1$*	$(19.0 \pm 0.5)\ 10^{-11}$	8.5 ± 0.5	9.0 ± 0.5
0.967$_3$	$(18.5 \pm 1.0)\ 10^{-11}$	9.2 ± 0.5	9.7 ± 0.5
0.486$_5$	$(6.2_5 \pm 0.4)\ 10^{-11}$	9.5 ± 0.5	10.0 ± 0.5
0.300$_9$	$(3.41 \pm 0.3)\ 10^{-11}$	10.0 ± 0.5	10.4 ± 0.5
0.194$_6$	$(2.3_5 \pm 0.2)\ 10^{-11}$	—	—
0.097$_3$	$(0.9 \pm 0.1)\ 10^{-11}$	—	—
0.100$_6$**	$(1.3_2 \pm 0.1)\ 10^{-11}$	—	—

* $[ClO_4^-] = 3.43$ M   ** $[ClO_4^-] = 0.31$ M

A normalized form of (13), $\log W(\log u)_{p'}$, was chosen which allows the simultaneous determination of p', K_1 and $K_{p'}$:

$$\log W(p') = \log (1 + p'u^{(p'-1)}) \qquad (14)$$

where

$$W = BZhK_1^{-1} \text{ and } \log u = \frac{1}{p'-1} \log (K_{p'}K_1^{-1}) - \log h \qquad (15)$$

If hypothesis (13) is valid then the data $\log (BZh)$ *versus* $(\log h)_B$ can be fitted to that member of the group of functions $W(p')$ which represents the correct value of p'. The most probable values of K_1 and $K_{p'}$ may be obtained by reading off, in the position of best fit, the displacement along the X axis, $\log u + \log h$, and that along the Y axis, $\log W - \log (BZh)$. Values of p', ranging from 2 to 12, were inserted into eqn. (14). For each value of B studied a satisfactory agreement could be found between the set of experimental points, $\log (BZh)$ *versus* $(\log h)_B$, and the functions $W(9)$ and $W(10)$; whereas successively increasing systematic deviations were obtained when p' was lower than 9 or higher than 10. The uncertainty of the data does not allow to make a distinction between $W(9)$ and $W(10)$.

We may thus conclude that our data may be explained by the formation of La_qOH and either $La_{q'}(OH)_9$ or $La_{q'}(OH)_{10}$ but not with any other mechanism involving only two values of p. The most probable $\log K_1$, $\log K_9$ and $\log K_{10}$ values, calculated with (14), are summarised in Table 4. With both pairs of constants (K_1, K_9) and (K_1, K_{10}) an excellent agreement could be attained with all sets of data.

Table 4. Homoligandic equilibrium constants calculated with self-medium method.

B M	$-\log K_1$	$-\log K_9$	$-\log K_{10}$
1.11_1*	9.72	71.10	78.69
0.967	9.73	71.45	79.08
0.486_5	10.20	72.87	80.61
0.300_0	10.47	74.06	81.87
0.194_6	10.63	74.95	81.90
0.097_3	11.03	76.66	84.81
0.100_0**	10.90	76.63	—

* $[ClO_4^-] = 3.43$ M.   ** $[ClO_4^-] = 0.31$ M.

It is not easy to give, on the basis of curve-fitting, a numerical estimate for the uncertainty of the calculated p' value, because, only a very narrow Z range is accessible, and the slope of the W curves becomes exceedingly high for $p' > 5$. An attempt was made therefore to examine systematically, how the calculation of p' is affected by the uncertainty of the data and by that of the numerical value of K_1.

Eqn. (13) may be put in the form

$$\log (BZ - K_1h^{-1}) = \log p' + \log K_{p'} - p' \log h \qquad (16)$$

where the left-hand side contains quantities directly known from the experiments, BZ and h, and K_1, which was calculated with reasonable accuracy previously. Two methods were employed for the estimation of p'. The first was a graphical method based on (16); p' was evaluated from the slope of the straight line which, according to the principle of least squares, best fitted a plot of log $(BZ-K_1h^{-1})$ *versus* $(\log h)_B$. The second was a numerical method; an even number of points $(2n)$ were considered for each value of B, and p' was calculated by

$$p' = \frac{\sum\limits_{1}^{n} y_i - \sum\limits_{n+1}^{2n} y_i}{\sum\limits_{1}^{n} x_i - \sum\limits_{n+1}^{2n} x_i}$$

where y_i and x_i denote a pair of corresponding values of $\log(BZ-K_1h^{-1})$ and log h. Both the upper and the lower limit of K_1, as given in Table 3, was used to calculate $(BZ-K_1h^{-1})$ from the experimental data. The effect of random experimental error was taken into account by varying the number of points $(2n)$ considered for a given value of K_1.

The measurements at $B = 0.1$ and 0.2 M could not be used to get a reliable value of p' by means of (16) because $(BZ-K_1h^{-1})$ becomes too small at these low lanthanum concentrations.

The p' values calculated using (16) (see Table 3) clearly indicate that, in complete agreement with the results found by curve-fitting, the most probable values of p' are 9 and 10. Moreover, the accuracy of the data seems to be sufficient to exclude the hypothesis that complexes with p' greater than 10 or less than 9 would be present in appreciable amounts.

Data of much higher accuracy than those we have been able to attain are required to decide between $La_{q'}(OH)_9$ and $La_{q'}(OH)_{10}$. It may be added, that the present accuracy would be quite sufficient to get more complete information concerning the composition of the hydrolysis products, if Z values up to, say, 0.1 could have been studied.

All the calculations in this section were made using approximation (5). The magnitude of the error introduced by this approximation was estimated by repeating the curve-fitting and the calculation of p' on the assumption that the species formed have the composition LaOH and $La_{p'}(OH)_{p'}$, *i.e.*

$$b = B(1-Z) \tag{17}$$

The results of the next section indicate that for those values of Z where the difference between (5) and (17) is of any importance, b is not likely to be significantly lower than $B(1-Z)$, thus (17) is a good approximation.

Functions corresponding to W (eqn. (14)) were calculated by assuming (17) and these were compared with the data. A satisfactory fit could be found only for $p' = 9$ and 10, and the K_1, K_9 and K_{10} values calculated using (17) coincided within the limits of experimental uncertainty with those obtained using (5).

The p' values calculated on the basis of (17) by an equation corresponding to (16) are given in Table 3. They are seen to be slightly higher than those found with (5), but the differences hardly exceed the experimental uncertainty.

Summarising these arguments we may infer that, for the low Z values in question, no appreciable error was introduced by using approximation (5). The main conclusions were not affected by the approximations employed in this section (eqns. (5) and (17)), since the final constants were obtained using the exact formulas (cf. section III).

II. The calculation of q, the number of lanthanum atoms present in the hydrolysis products

To find q, we must compare data obtained at different values of B, because in our solutions b is always practically equal to B. Such a comparison involves some uncertainty, since we are not able to estimate the variation of the activity factors caused by the replacement of a large part of the inert cations (Li^+) by the reacting ions. In the following calculations the rough approximation was made that the changes in the activity factors are negligible when B varies from 0.097 to 0.967 M while $[ClO_4^-]$ is kept constant at the value $3B + [Li^+] + H$.

The calculations are based on the analysis of the functions $K_1(B)$, $K_9(B)$ and $K_{10}(B)$ which form power series; values of these functions, as obtained by the self-medium method, are tabulated in Table 3. According to (10) K_1 is equal to

$$K_1 = B\,\beta_{1,1} + B^2\,\beta_{1,2} + \ldots \tag{18}$$

As Fig. 3 shows, a plot of $K_1 B^{-1}$ approximates closely to a straight line. This fact indicates according to (18) that the species $LaOH^{2+}$ and La_2OH^{5+} are formed. From the intercept and slope of the best line, obtained by the method of least squares, we have calculated the equilibrium constants

$$\log \beta_{1,1} = \log\{[LaOH^{2+}]\,h\,b^{-1}\} = -10.1 \pm 0.1$$

and

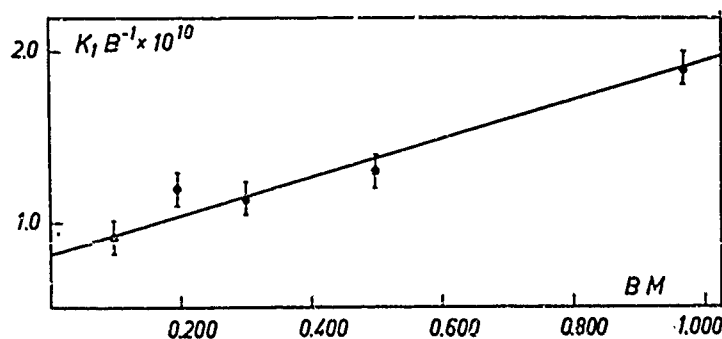$$\log \beta_{1,2} = \log\{[La_2OH^{5+}]\,h\,b^{-2}\} = -10.0 \pm 0.3$$

Fig. 3. $K_1 B^{-1}$ (eqn. (18)) as a function of B. The straight line represents the equation $K_1 B^{-1} = 8.2 \times 10^{-11} + 1.14 \times 10^{-10}\ B$.

The uncertainties of the $\log \beta_{1,1}$ and $\log \beta_{1,2}$ values given represent the maximal deviations. Since the self-medium data could be equally well interpreted with K_9 and K_{10}, we have to consider both of the two functions

$$K_9 = \Sigma B^{q_1} \beta_{9,q_1} \quad \text{and} \quad K_{10} = \Sigma B^{q_k} \beta_{10,q_k} \tag{19}$$

where q_1 and q_k may take a series of values.

Each of the plots $\log K_9(\log B)$ and $\log K_{10}(\log B)$ could be well represented with a straight line, which had a slope of 5 for $\log K_9(\log B)$ and of 6 for $\log K_{10}(\log B)$. These results can be explained in the simplest way by assuming the formation of $La_5(OH)_9^{6+}$ (for $p = 9$) and $La_6(OH)_{10}^{8+}$ (for $p = 10$). The calculations are illustrated in Fig. 4a where $(\log K_9 - q_1 \log B)$ is plotted against B for $q_1 = 4$, 5 and 6, and in Fig. 4b where $(\log K_{10} - q_k \log B)$ is plotted against B for $q_k = 5$, 6 and 7. It is seen, that $\log \beta_{9,5}$ and $\log \beta_{10,6}$ prove to be constant within the limits of experimental uncertainty, whereas a great systematic trend is found for the adjacent q values. Moreover, the deviation from constancy changes sign when q passes through 5 and 6. We can read off from the figures the values

$$\log \beta_{9,5} = \log \{[La_5(OH)_9]h^9 b^{-5}\} = -71.4 \pm 0.2$$

or

$$\log \beta_{10,6} = \log \{[La_6(OH)_{10}] h^{10} b^{-6}\} = -78.8 \pm 0.2$$
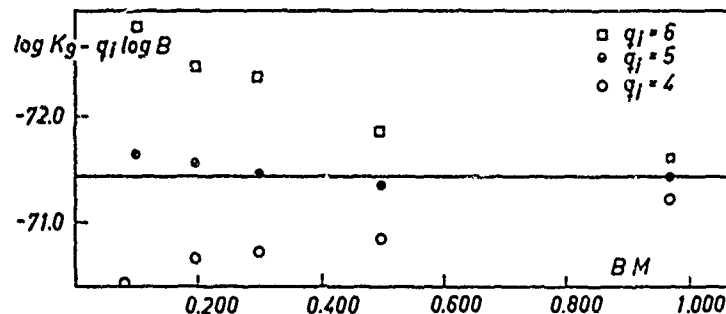
which may be regarded as first approximations.

Fig. 4a. $\log K_9 - q_1 \log B$ (eqn. (19)) as a function of B for $q_1 = 4$, 5 and 6. The points for $q_1 = 4$ have been shifted vertically by $+0.2$ and those for $q_1 = 6$ by -0.2 units.
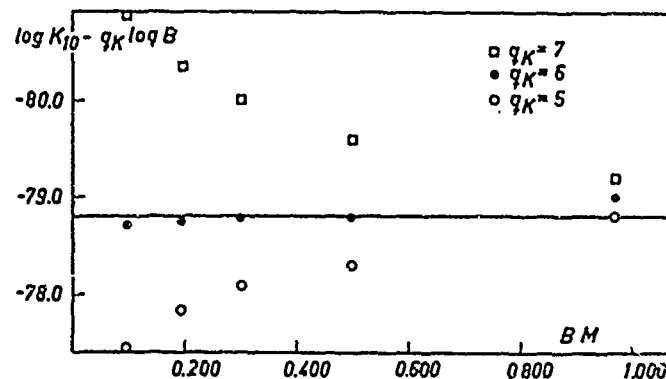

Fig. 4b. $\log K_{10} - q_k \log B$ (eqn. (19)) as a function of B for $q_k = 5$, 6 and 7. The points for $q_k = 5$ have been shifted vertically by $+0.2$ and those for $q_k = 7$ by -0.2 units.

III. Comparison of the data with normalised projection maps

In the preceding section probable values for the q—s and the $\beta_{p,q}$—s were derived by analysing the dependence of the overall equilibrium constants, K_p, on B. The conclusions drawn on the basis of these calculations must be regarded as preliminary ones, because they are appreciably influenced by the uncertainty of the numerical values of the K_p—s. Moreover, the results of section II are in such a remote contact with the data, that it is difficult to estimate the effect of the experimental uncertainty.

In order to check the previously estimated q and $\beta_{p,q}$ values a plot covering the complete set of the experimental data was compared with groups of normalised functions. Since the same plot may be compared with groups of functions representing different hypotheses, it may be inferred whether the experimental accuracy is sufficient to make a decision between these different hypotheses. This highly effective way to analyze experimental data when three variables must be considered, has been proposed by Sillén [14]. The method of calculation described in a previous work [15] was followed closely.

First, the experimental $Z(\log h)_B$ data were recalculated to the form $\log B(\log B - 2\log h)_Z$, by interpolation. A plot of $\log B(\log B - 2\log h)_Z$ was then compared with two groups of normalised functions, both of which were calculated by assuming the formation of three species. For the first group the hypothesis was made that the species have the composition $LaOH^{2+}$, La_2OH^{5+} and $La_5(OH)_9^{6+}$ (hypothesis 5,9), whereas for the second the combination $LaOH^{2+}$, La_2OH^{5+} and $La_6(OH)_{10}^{8+}$ was chosen (hypothesis 6, 10).

The essential steps of the calculation will be described in some detail for the first hypothesis only; a closely analogous method was followed for the second.

We started with the fundamental equations

$$B = b(1 + \beta_{1,1}h^{-1} + 2\beta_{1,2}bh^{-1} + 5\beta_{9,5}b^4h^{-9}) \tag{20}$$

and

$$BZ = b(\beta_{1,1}h^{-1} + \beta_{1,2}bh^{-1} + 9\beta_{9,5}b^4h^{-9}) \tag{21}$$

Introducing the new variables

$$\beta_{1,1}h^{-1} = a, \quad (\beta_{9,5}\beta_{1,1}^{-1})^{1/4}bh^{-2} = u \tag{22}$$

and

$$\beta_{1,2}(\beta_{1,1}^5\beta_{9,5}^{-1})^{1/4} = \gamma \tag{23}$$

equs. (20) and (21) can be written

$$B = (\beta_{1,1}^9\beta_{9,5}^{-1})^{1/4}a^{-2}u(1 + a + 2\gamma ua^{-1} + 5u^4a) \tag{24}$$

$$Z = \frac{a + \gamma ua^{-1} + 9u^4a}{1 + a + 2\gamma ua^{-1} + 5u^4a} \tag{25}$$

Eliminating a from (24) and (25), and keeping Z and γ constant, B can be expressed as a function of the single variable u

$$B = B(u)_{Z,\gamma} \tag{26}$$

We then constructed, on the basis of (26), (25) and (24), the normalised functions $Y(u)_Z$ and $X(u)_Z$; the calculations were made with the aid of a Ferranti-Mercury high-speed computer.

$$Y = \log u - 2 \log a + \log (1 + a + 2\gamma u a^{-1} + 5u^4 a) = \log B - \tfrac{9}{4} \log \beta_{1,1} + \tfrac{1}{4} \log \beta_{9,5}$$

and   (27)

$$X = Y + 2 \log a = \log B - 2 \log h - \tfrac{1}{4} \log \beta_{1,1} + \tfrac{1}{4} \log \beta_{9,5} \qquad (28)$$

Y and X, which represent the normalised form of $\log B$ and $(\log B - 2 \log h)$, were calculated for a series of Z values ranging from 0.003 to 0.015. Log γ values ranging from -4.20 to -4.90 were considered. Each group of functions calculated with a particular γ value was superimposed on the plot $\log B(\log B - 2 \log h)_Z$. The best agreement was obtained with $\log \gamma = -4.70$. The differences $X - (\log B - 2 \log h)$ and $Y - \log B$ were read off, in the position of best fit, and then the most probable values of the constants $\log \beta_{1,1}$, $\log \beta_{1,2}$ and $\log \beta_{9,5}$ could be calculated using (23), (27) and (28). The results are given in Table 5.

Table 5. Survey of the calculated equilibrium constants, $\beta_{p,q}$.

Method	$-\log \beta_{1,1}$	$-\log \beta_{1,2}$	$-\log \beta_{9,5}$	$-\log \beta_{10,6}$
Projection map Hypothesis (5,9) $LaOH^{2+}$, La_2OH^{5+} and $La_5(OH)_9^{6+}$	10.1 ± 0.1	$9.9_2 \pm 0.1$	$71.4_4 \pm 0.1$	—
Hypothesis (6,10) $LaOH^{2+}$, La_2OH^{5+} and $La_6(OH)_{10}^{8+}$	10.1 ± 0.1	$9.9_7 \pm 0.1$	—	$78.7_6 \pm 0.1$
$K_p(B)$ Eqn. (18)	10.1 ± 0.15	10.0 ± 0.3	—	—
Eqn. (19)	—	—	$71.4_5 \pm 0.2$	78.8 ± 0.2
Probable value	10.1 ± 0.1	$9.9_5 \pm 0.1$	$71.4_5 \pm 0.1$	$78.7_6 \pm 0.1$

When the data were compared with normalised curves representing hypothesis (6, 10) the best agreement was found for the $\log \beta_{1,1}$, $\log \beta_{1,2}$ and $\log \beta_{10,6}$ values shown in Table 5.

The results of all these calculations are illustrated in Fig. 5, which shows that the experimental data can be represented equally satisfactorily by hypothesis (5,9) or (6,10), using the constants given in Table 5. It is seen that the values of the equilibrium constants obtained in section II (shown in Table 5) are in good agreement with those calculated on the basis of the normalised functions (27) and (28).
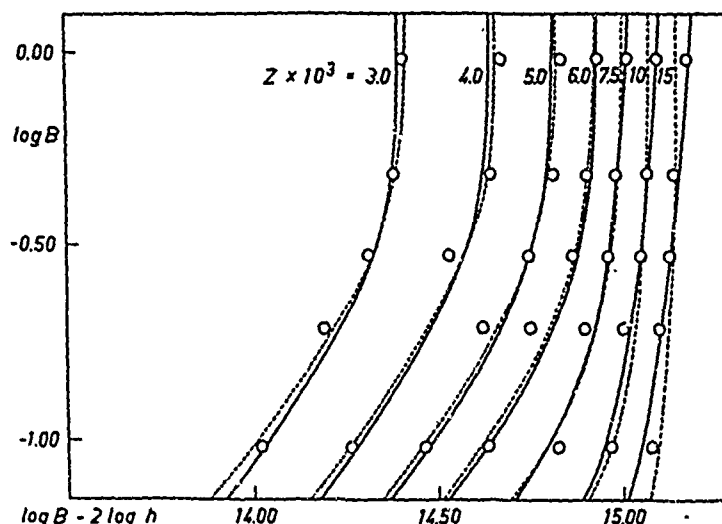
Fig. 5. log B as a function of (log B — 2 log h) for Z values 0.003 to 0.015. Circles: experimental points. The full-drawn curves have been calculated with hypothesis (5,9), the dotted curves with hypothesis (6, 10). The constants given in Table 5 were used.

Finally we may consider Fig. 1. The full-drawn curves represent hypothesis (5,9), the dotted curves hypothesis (6,10). Both of them seem to describe satisfactorily the experimental data of present accuracy.

It must be pointed out that our conclusions concerning the number of lanthanum atoms present in the hydrolysed species, q, include the uncertainty caused by the unknown variation of the activity factors, whereas this complication is of no importance for the determination of p (the number of OH groups bound to the hydrolysis products). We are inclined to believe that the proposed values of q are not far from the correct ones, and that the main effect of the variation of the activity factors is an increased uncertainty in the numerical values of the equilibrium constants $\beta_{p,q}$. There is some experimental evidence [16] which suggests that when the inert cation is largely replaced by the reacting cation, in solutions where [ClO$_4^-$] = 3 M, the individual activity factors of the reacting ions change considerably, but certain combinations of them vary only slightly, e.g. $f(In^{3+})/f(H^+)^{-3}$.

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